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Activation and reaction volumes of the reactions of o- and p-nitrophenylsulfenyl chlorides with styrene and cyclohexene in some solvents

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Abstract

The effect of hydrostatic pressure below 1000 kg cm-2 on the rate of reactions of o-and p-nitrophenylsulfenyl chlorides with styrene and cyclohexene was studied. The activation and reaction volumes (cm3 mol-1) for the reactions of o-nitrophenylsulfenyl chloride with styrene in acetonitrile (-23.1 and -23.6), 1,2-dichloroethane (-29.2 and -24.7), chlorobenzene (no, -20.2), and anisole (-25.1 and -21.2) and for the reaction of p-nitrophenylsulfenyl chloride with styrene in carbon tetrachloride (-39.5±1.5 and -22.0) were determined. In carbon tetrachloride the activation volumes for the reactions of cyclohexene with o-and p-nitrophenylsulfenyl chlorides (-37.7±2.0 and -40.9±1.2 cm 3 mol-1, respectively) are almost the same and coincide with the data for the reactions with styrene. The considerable decrease in the volume of the transition state in the nonpolar solvent is considered as a consequence of the enhanced electrostriction of carbon tetrachloride in the solvate sphere of the transition state of the reaction, which excludes the nonpolar transition state of the sulfuran type.

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Keywords

Activation volumes, Mechanism, O-nitrophenylsulfenyl chloride, Reaction volumes, Solvent effect, Styrene